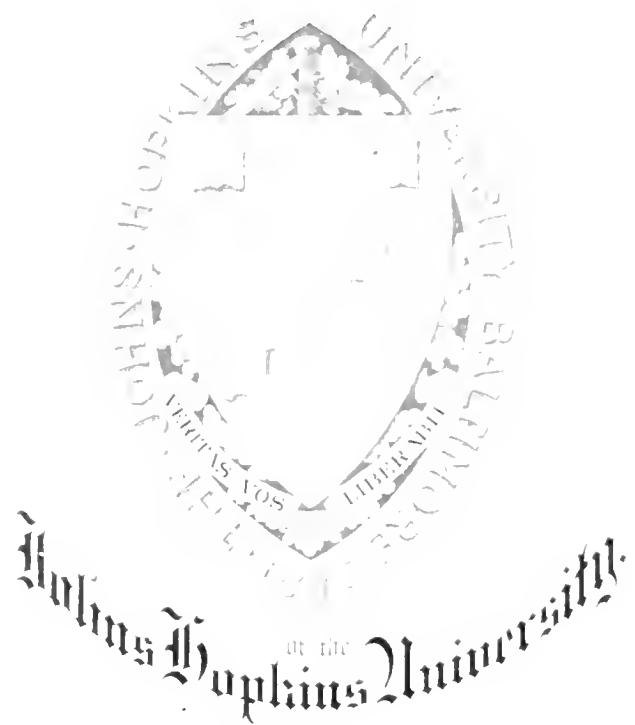


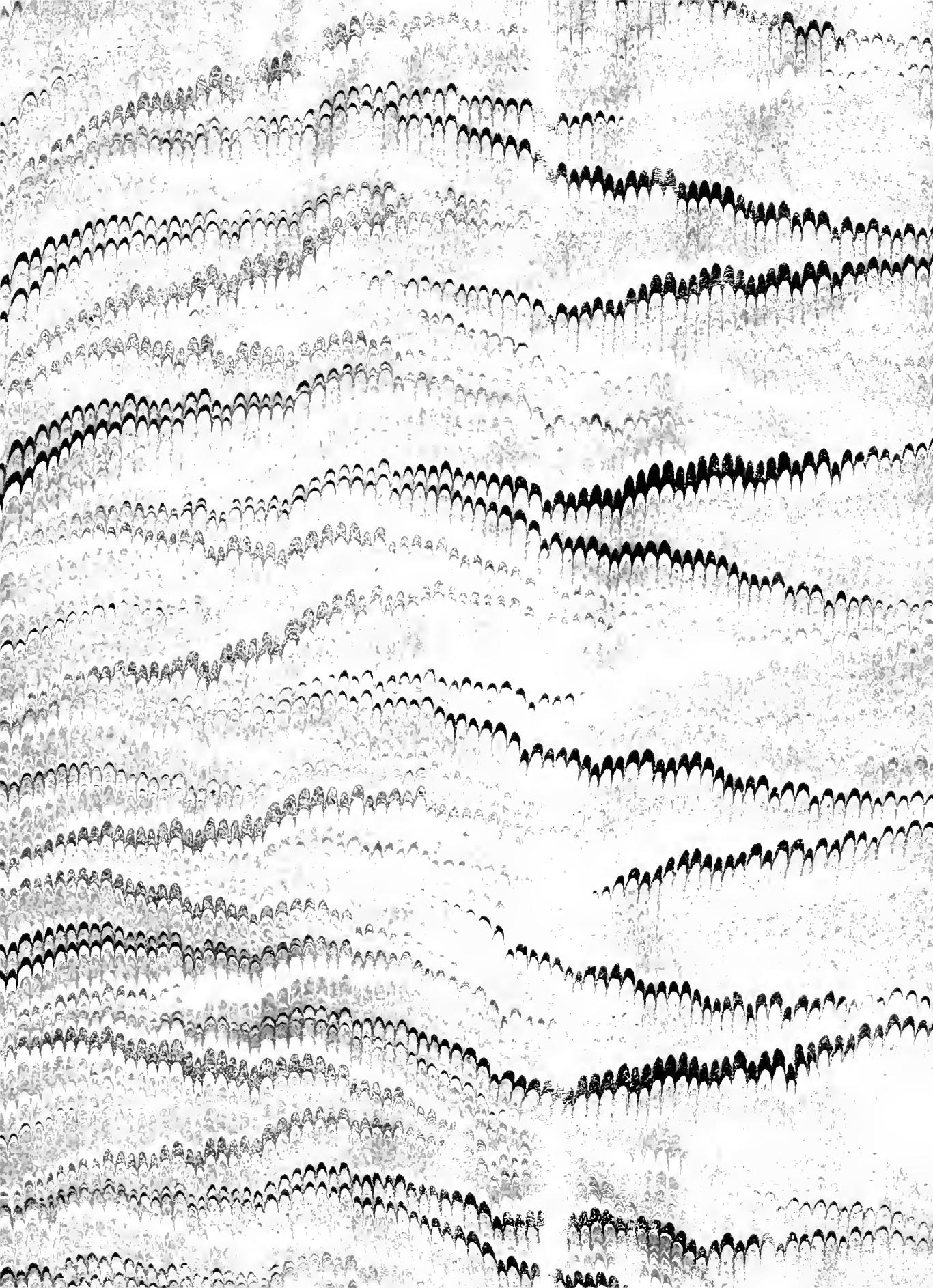
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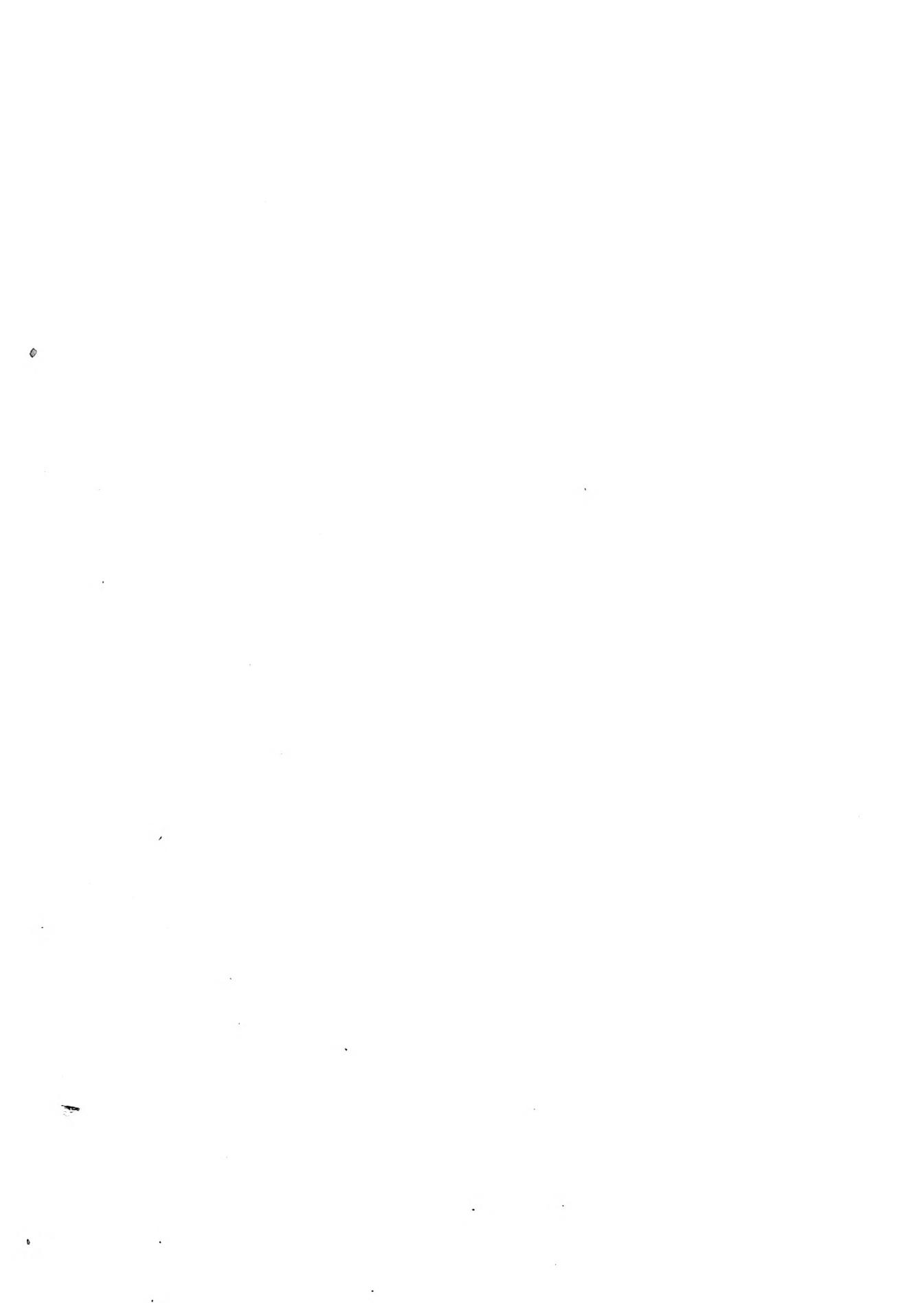
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A STUDY OF THE CONDUCTIVITY OF CERTAIN SALTS
IN WATER, METHYL, ETHYL, AND PROPYL ALCOHOLS
AND
MIXTURES OF THESE SOLVENTS.

DISSERTATION
SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE
JOHN'S HOPKINS UNIVERSITY IN CONFORMITY WITH THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY.

-BY-

CHARLES FOWLER LINDSAY.

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A STUDY OF THE CONDUCTIVITY OF CERTAIN SALTS IN
WATER, METHYL, ETHYL, AND PROPYL ALCOHOLS
AND MIXTURES OF THESE SOLVENTS.

Part I. Historical.

Ever since the birth of the theory of Electrolytic Dissociation of Arrhenius and the perfection of the Kohlrausch method for the measurement of the conductivity of solutions the determination of the dissociation of electrolytes in aqueous solution has been the subject of almost endless investigation. The work was however almost exclusively confined to aqueous solutions due to the fact that water is a solvent for so many substances, that it is a very good dissociant, and that it can be purified with ease.

But during the last few years the measurement of dissociation has been extended, to a greater or less extent, to solutions in a great many solvents both Inorganic and Organic, in some cases with very interesting results.

The study of these non-aqueous solutions has led to the comparison of the dissociating power of the various solvents and this in turn has been the cause of several generalizations striving to connect dissociating power with other physical and chemical properties.

J.J.Thomson (1) and Nernst (2) have sought to connect the dissociating power of a solvent with its dielectric constant.

Nernst says "The greater the dielectric constant of a medium the greater becomes its electrolytic dissociation of dissolved substances under exactly similar conditions."

J.J.Thomson after showing that molecules condensed on the surface of a conducting sphere will be completely dissociated goes on to say, "The same effect would be produced by a substance possessing a very large specific inductive capacity. Since water is such a substance it follows if we accept the view that the forces between the atoms are electrical in their origin, that when the molecules of a substance are in solution the forces between them are very much less than they are when the molecule is free and in the gaseous state."

Brühl (3) shows that while certain organic bodies as the oximes and the alcohols exist in a polymerized state in hydrocarbons, chloroform, or carbon bisulphide solution, the molecular complexes are more or less broken down in water solution and to a less extent in alcohols, ethers, esters, ketones and phenols. All of these also exert a more or less electrolytic dissociating action. They all contain oxygen as a bivalent element. According to his theory of the tetravalence of oxygen they are unsaturated compounds and it is to this unsaturation that he ascribes dissociating action.

(1) Phil. Mag., 36, 320.

(2) Ztschr. physikal. Chem., 13, 531.

(3) Ibid., 18, 514; 27, 310; 30, 1.
Ber. d. chem. Ges., 28, 2847, 2866; 30, 163.

He also attributes the dissociating power of solvents containing nitrogen to the fact that in these compounds nitrogen exists as a triad while it has the power of becoming pentavalent. He predicted dissociating power for compounds containing trivalent nitrogen including the hydrazines, the amines, the diazo compounds and liquid hydrocyanic acid, and even for unsaturated compounds other than of nitrogen as the trichlorides of arsenic and phosphorus, the mercaptans and alkyl sulphides. A prophecy that has been born out to some extent at least by the later work of Walden. In his last paper Brühl has sought rather to connect dissociating power with a high dielectric constant and with the tautomerising power of the solvent.

Ciamician (1) has concluded that dissociating power is a chemical function of the substance and that those substances which resemble water chemically as methyl and ethyl alcohol should have the greatest dissociating power.

Konowalow (2) from a study of the conductivity of the compounds which amines form with acids holds that only those solutions conduct where there is a chemical action between the solvent and the dissolved substance.

Dutoit and Aston (3) have advanced the idea that dissociating power is related to the amount of the polymerization of the solvent. Water and the alcohols which are good diss-

(1) Ztschr. physikal. Chem., 6, 403.

(2) Wied. Ann., 49, 733.

(3) Compt. Rend., 125, 240. See also Dutoit and Friderich

Bull. soc. chim., (3), 19, 325. and Crompton Jour. Chem. Soc. 71, 925.

-ociants are also polymerized molecules as shown by the surface tension method of Ramsay and Shields.(1)

Donnan (2) says. " In a solution in which the solute is more or less ionized one might suppose the ions to be surrounded by clusters of solvent-molecules which had, so to speak, condensed round them and opposed an obstacle to their recombination. Now one might suppose this state of things as being caused by some sort of specific attraction between the solvent molecules and electricity, i.e. the electrons or electrical charges which are associated with the ions. Were this the case, one might expect this specific attraction to manifest itself in other ways. For example, if electrical nuclei were present in or were produced by any means in air which was saturated with the vapor of an ionizing liquid then it would be just possible that the specific attraction referred to above might help to produce condensation of the vapor around these nuclei under suitable conditions; i.e. if the vapor were supersaturated by a sudden adiabatic expansion. If the liquid in question did not act as an ionizing solvent, it would be natural to expect that the condensation just alluded to would only occur when the vapor entered the really unstable (labile) region, or at any rate would only be produced by a much higher degree of supersaturation." From his experiments however he does not feel warranted in drawing any definite conclusion.

(1) Ztschr. phys. Chem., 17, 433.

(2) Phil. Mag. (6) 15, 305.

In going into a more detailed account of the results which have been the cause of the above generalizations I will consider the work done, first in Inorganic Solvents, second in Organic Solvents and third in Mixed Solvents.

INORGANIC SOLVENTS.

Water has always been regarded as the best dissociant, but within the last few months another solvent, liquid hydrocyanic acid, has been found to give greater dissociation.

Hydrocyanic Acid: - Schlundt (1) had measured the dielectric constant of liquid hydrocyanic acid and found the very large value of 95 at 21° C. a value which exceeded that of water which is 80 at the same temperature. On account of this it was of much importance as bearing on the Nernst-Thomson theory of dissociation, that measurements of the conductivity of solutions in this solvent be made. This has been done by Centnerszwer (2) with the result of showing that not only do solutions in hydrocyanic acid show greater conductivity but the dissociation is also greater than in water. The substances worked with were Potassium Iodide and Trimethylsulphur Iodide. Their conductivity at 0° was about the same as value as the conductivity of aqueous hydrochloric acid at 25°.

(1) Journ. Phys. Chem., 5, 157.

(2) Journ. Russ. Phys. Chem. Soc., (3), 548, - 549.

Ztschr. physikal. Chem., 39, 217.

Water. The dissociation of a great number of substances in aqueous solution has been determined by a variety of methods including the conductivity method of Kohlrausch (1), the freezing point method of Jones (2) Loomis (3) and others, and the solubility method as worked out by Ternst (4) and Noyes (5). A result of this work has been to show that for a strong acid or a strong base or a salt of a strong acid and a strong base that at a dilution of about one thousand litres the dissociation is practically completed. In most cases however it is impossible to determine the value of μ_x directly by the conductivity method, since the dilution at which complete ionization is reached is so great as to preclude the application of the conductivity method. The best that we can do under these circumstances is to compare the values of μ_v at varying dilution with the corresponding values for μ_v in water solution. In this way an approximation to the dissociation power of various solvents can be obtained.

(1) Wied. Ann., 26, 160.

(2) Ztschr. physikal. Chem., 11, 110 and 529; 12, 523.

(3) Wied. Ann., 51, 80; 7, 495 and 591; 60, 523.

(4) Ztschr. physikal. Chem., 4, 372.

(5) Ibid., 241; 2, 603; 12, 162; 14, 120.

Ammonia. Several years ago Cady (1) noticed that solutions of salts in liquid ammonia conduct the current. Goodwin and Thomson (2) made some measurements of the conductivity of such solutions while at their work on the dielectric constant of liquid ammonia. The best work however on this subject is due to Franklin and Kraus (3). They measured the conductivity of potassium bromide and nitrate, sodium bromide and bromate, ammonium chloride and nitrate, silver iodide and cyanide, besides other inorganic salts and organic compounds over very great changes in dilution.

A direct comparison of the values of the conductivities in liquid ammonia with similar values in water shows that the former are much larger than the latter. This however does not necessarily mean a larger dissociation, for the conductivity is dependent on two factors namely the dissociation and the velocities of the ions. The percentage dissociation, ($\chi = \frac{u_1}{u_\infty}$) is larger in water than in ammonia, and hence the large conductivity of solutions in liquid ammonia is due rather to the high velocity of the ions than to the large number present.

(1) Journ. Phys. Chem., 1, 707.

(2) Phys. Rev., 8, 38.

(3) Am. Chem. Journ., 23, 277; 24, 83.

Nitric Acid. The only work on solutions in nitric acid is that of Bouthy (1) who has measured the conductivity of certain alkaline nitrates when dissolved in nitric acid. The conductivities are nearly as great as in water but the work is too fragmentary to permit the drawing of comparisons between the dissociating power of nitric acid and of water. It is however in all probability great.

Sulphur Dioxide. Walden and Centnerszwer (2) have very recently published the results of a very extensive investigation on sulphur dioxide as a solvent. This is an extension of the older work of Walden (3). They have found by an investigation of the conductivity of nineteen salts consisting of iodides bromides chlorides and sulphonocyanates of inorganic and organic bases, first that while in aqueous solution the molecular conductivity at 25° of monobasic halogen salts generally lies between 100 and 140 the corresponding values in sulphur dioxide vary between 3 and 157; second that Kohlrausch's law of the independent migration of the ions does not hold for sulphur dioxide solutions. They have also shown by a series of conductivity measurements at different temperatures between -78 and +157 namely the melting and critical temperatures of sulphur dioxide that

(1) Compt. Rend., 106, 595.

(2) Ztschr. physikal. Chem., 39, 513.

(3) Ber. d. chem. Ges., 32, 2862.

the molecular conductivity at first increases passes through a maximum and then diminishes towards the critical temperature. This is seen to be just what would be expected from the polymerized solvent theory of Dutoit and Aston, for as the temperature increases the association of the solvent diminishes and this would be expected to have a retarding action on the ionization. They have also determined the molecular weights of a number of electrolytes (salts) in liquid sulphur dioxide reaching the remarkable result that many of these salts show a molecular weight greater than normal or what is the same thing the values of the Van't Hoff "i" is less than unit. This they endeavor to show to be due to the fact that in addition to the electrolytic dissociation an association (not electrolytic) takes place in the sulphur dioxide solutions. Facts of a similar kind to the maximum values in the temperature-conductivity curve were, as well as the abnormal values of the Van't Hoff "i", noticed by Franklin and Kraus (1) in their work on liquid ammonia.

The remaining work on inorganic solvents is almost entirely due to Walden (2). He has investigated the solvent and ionizing power of the following compounds of:-

(1) Am. Chem. Journ., 20, 830; 24, 83.

(2) Ztschr. Anorg. Chem., 25, 219; 28, 371.

Boron, BCl_3

Phosphorus, PCl_5 , PBr_3 , and POCl_3 .

Arsenic, AsCl_3 .

Antimony, SbCl_3 , and SbCl_5 .

Silicon, SiCl_4 .

Tin, SnCl_4 .

Sulphur, S_2Cl_2 , SOCl_2 , SO_2Cl_2 , and SO_3 .

and liquid Bromine. Of these sulphur ^{mono}~~chloride~~, sulphuryl chloride, thionyl chloride, phosphorus oxychloride, arsenic trichloride, and antimony trichloride show considerable ionizing power while solutions in the remainder exhibit but the very slightest conductivity. In his next paper he adds a study of arsenic trioxide, chlor-sulphuric acid sulphuric acid, and sulphuric acid dimethylester. All of these show a strong tendency to ionize dissolved electrolytes.

What is important to notice in this work of Walden's is that there appears to be no connection between dissociating power and chemical constitution. Antimony pentachloride does not dissociate electrolytes while the trichloride does to a very marked extent; on the other hand phosphorus trichloride does not dissociate while the oxychloride does. It is thus evident that among the inorganic solvents at least from a knowledge of the dissociating power of one solvent nothing can be judged as to the power of substances closely related chemically.

Of the remaining work but little need be said. Oddo (1) has also shown that phosphorus oxychloride strongly ionizes. Tolloczko (2) as well as Arelli and Bassani (3) have worked with the halides of arsenic and antimony, showing them to have ionizing power. Landenborg and Lincoln (4) have studied solutions of ferric chloride, antimony trichloride, bisuth trichloride and mercuric chloride in phosphorus trichloride and arsenic trichloride with results confirmatory of the above named investigators. Centnerszwer (5) is authority for placing cyanogen along the solvents which do not dissociate. Frankland and Farmer (6) have also shown that nitrogen peroxide does not dissociate. Skilling (7) has also shown the same for liquid hydrogen sulphide.

I give the following table showing for inorganic solvents what relations exist between dissociating power, dielectric constant and the association factor.

- (1) Atti R. Accad. dei Lincei Roma, (1), 10, 451.
- (2) Ztschr. physikal. Chem., 30, 705.
- (3) Atti R. Accad. dei Lincei Roma, (2), 10, 275.
- (4) Journ. Phys. Chem., 39, 217.
- (5) Ztschr. physikal. Chem., 39, 217.
- (6) J.C.S., 79, 1356.
- (7) Am. Chem. Journ., 26, 383.

Solvent.	Tielectric Constant.	Association Factor.	Considered as:-
Hydrocyanic acid.	95	?	saturated
Water.	81.12	3.7	saturated
Ammonia.	16.2	1.0	unsaturated
Sulphur dioxide.	13.75	1.0	unsaturated
Nitric acid.	?	1.7-1.9	saturated
Arsenic trichloride.	12.35	?	unsaturated
Arsenic tribromide.	?	?	unsaturated
Phosphorusoxy-chloride.	13.9	1.00	saturated
Antimony trichloride.	35.2	?	unsaturated
Thionylchloride.	9.05	1.08	unsaturated
Sulphurylchloride.	9.15	0.97	saturated
Sulphuric acid-dimethylester.	?	?	saturated
Chlorsulphuric acid.	?	?	saturated
Sulphuric acid.	?	52.	saturated
Sulphurdichloride.	4.8	0.95-1.05	unsaturated

Inorganic solvents which do not dissociate.

Bromine.	3.1	1.2-1.3	saturated
Cyanogen.	2.52	?	saturated
Sulphur trioxide.	3.56	?	saturated
Boron trichloride.	?	?	saturated
Phosphorus trichloride	3.36	1.02	unsaturated
Phosphorus tribromide.	?	?	unsaturated
Antimony pentachloride	3.78	?	saturated
Silicon tetrachloride.	?	1.06	saturated
Tin tetrachloride.	3.2	?	saturated
Sulphuretted hydrogen.	?	?	saturated
Nitrogen peroxide.	?	?	saturated

The values for the association factors are taken from the researches of Ramsay and Shields (1) and Ramsay and Aston(2). While those for the dielectric constant are almost wholly taken from the work of Turner (3).

(1) Ztschr. physikal. Chem., 17, 435.

(2) J.C.S., 60, 167.

(3) Journ. Phys. Chem., 5, 503.

ORGANIC SOLVENTS.

Hydrocarbons. Kahlenberg and Lincoln (1) have shown that solutions of ferric chloride in a large number of hydrocarbons do not conduct the current; while Kablukoff (2) showed that the conductivity of hydrochloric acid in benzene, xylene, and hexane is very small. This is in perfect accord with what would be expected from the fact that non-electrolytes dissolved in hydrocarbons tend in a number of cases to give a complex molecular weight when determined by the boiling or freezing point methods.

Alcohols. When we come to study the work done in solutions in the alcohols we find that already a considerable amount has been done especially in the case of the two lowest members of the aliphatic series. Fitzpatrick (3) studied the conductivities of calcium nitrate, lithium nitrate, lithium chloride and calcium chloride in methyl alcohol, and found values which though less than in water were very ⁿconsiderable. Hartwig (4) measured the conductivity of formic, acetic, and butyric acids in methyl alcohol. Paschow (5) studied the conductivities in methyl alcohol of potassium iodide, cadmium iodide, calcium nitrate, and potassium and sodium acetates. Völlmer (6) has

- (1) Journ. Phys. Chem., 5, 12.
- (3) Phil. Mag., 24, 378.
- (2) Ztschr. physikal. Chem., 4, 429.
- (4) Wied. Ann., 33, 58; 43, 838.
- (5) Charkow., 1892.
- (6) Wied. Ann., 52, 328.

worked out the conductivities of potassium and sodium iodides, potassium and sodium acetates, and lithium chloride in methyl alcohol, for a considerable range of dilution.

Holland (1) studied the effect of non-electrolytes on the conductivity in methyl alcohol of potassium, sodium, calcium, lithium and ammonium nitrates and sodium chloride.

Carrara (2) carried out by far the most extensive investigation of salts in methyl alcohol which has yet been made. He measured the conductivities of the following substances at various dilutions: potassium chloride, bromide, iodide, methydate; sodium chloride, iodide, methydate, acetate; lithium chloride; ammonium chloride, bromide, iodide, fluoride; tetraethylammonium chloride, bromide, iodide; tetramethylammonium iodide; triethylamine, diisopropylamine, and a number of sulphur derivatives. Kerler (3) working in Beckmann's laboratory has determined the conductivities of lithium and calcium chlorides, lithium, sodium, and barium bromides, potassium iodide, ammonium nitrate, and potassium acetate. The conductivity of mercuric iodide in methyl alcohol was measured by Cattaneo (4); Schall (5) determined the conductivity of hydrochloric, picric, oxalic, and dichloracetic acids in methyl

(1) Wied. Ann., 50, 263.

(2) Gazz. chim. ital., 26, (1), 119.

(3) Dissertation, Erlangen, 1894.

(4) Rend. R. Acc. Linc. Roma, 1895.

(5) Ztschr. physikal. Chem., 14, 701.

alcohol; Kablukoff (1) also studied the conductivity of hydrochloric acid in methyl alcohol; and Kahlenberg and Lincoln (2) measured the conductivity of ferric chloride and antimony trichloride in this solvent. The most satisfactory work on the whole which has ever been done on the conductivity of solutions in methyl alcohol is that of Zelinsky and Krapiwin. (3) Their work included a number of salts in pure methyl alcohol, as well as in a mixture of this solvent and water, as we shall see later. They used in their work potassium bromide, and iodide, ammonium bromide and iodide, cadmium iodide, tetramethylammonium bromide and iodide, tetraethylammonium iodide, a number of the substituted amines and sulphines, diethyl- and triethylstannic iodides, "fumaroid" dimethylsuccinic acid, oxalic acid, iodic acid, and trichloracetic acid.

Jones has applied (4) his boiling point apparatus to determine the dissociation of salts in methyl alcohol. The salts used were potassium sodium and ammonium bromides, potassium sodium and ammonium iodides, potassium and sodium acetates, and calcium nitrate. The dissociation in methyl alcohol, as found by the boiling point method is about two-thirds of that in water under the same conditions.

(1) Ztschr. physikal. Chem., 4, 429.

(2) Journ. Phys. Chem., 3, 26.

(3) Ztschr. physikal. Chem., 21, 35.

(4) Phil. Mag., ^{27.4} 21, 35. 34, -.

Ethyl Alcohol.: - A considerable amount of work has also been done in ethyl alcohol. The conductivity of the following substances has been determined by Fitzpatrick (1) calcium chloride calcium nitrate, lithium chloride, lithium nitrate, mercuric, magnesium, and ferric chlorides. Hartwig (2) has determined the conductivity of formic, acetic, and butyric acids in alcohol. Vicentini (3) worked on the chlorides of ammonium, lithium, magnesium, calcium, cadmium, zinc, and copper. Cattaneo (4) has studied the conductivities of ferrous ferric and mercuric chlorides, cadmium bromide and iodide. He found that these substances have a negative temperature coefficient of conductivity. Vollmer used a larger number of salts in ethyl alcohol than he did in water (5). These were potassium and sodium iodides, potassium and sodium acetates, sodium, lithium, and calcium chlorides, and calcium and silver nitrates. Kawalki (6) by a comparison of the rates of diffusion of a series of salts in water and in ethyl alcohol showed that the rates of diffusion in the two solvents bear the same relation to one another as the maximum molecular conductivities in the two solvents. Reference should be made to the work of Paschkow.

(1) Phil. Mag., 24, 378.

(2) Wied. Ann., 33, 58; 43, 838.

(3) Biebl. Wied. Ann., 9, 131.

(4) Ibid., 18, 219, 365.

(5) Wied. Ann., 52, 328.

(6) Ibid., 52, 324.

(1), who measured the conductivities in ethyl alcohol of potassium and cadmium iodides, potassium and sodium acetates, and calcium nitrate; of Schall (2) who measured picric, oxalic, and dichloracetic acids; of Wildermann (3) who studied the conductivities of di- and trichloracetic acids; of Kahlenberg and Lincoln (4), who worked with ferrichloride and antimony trichloride in ethyl alcohol; and of Kablukoff (5), who has measured the conductivity of hydrochloric acid in ethyl alcohol.

Jones (6) has measured the dissociation of a number of salts in ethyl alcohol using the boiling point method. These include potassium and sodium iodides, sodium and ammonium bromides, potassium and sodium acetates, and calcium nitrate. These salts were found to be dissociated by ethyl alcohol to from one-third to one-fourth the extent that they are dissociated in water at the same dilution. It should be observed however that dissociation as measured by the boiling point method would not seem to be directly comparable with dissociation as measured by the conductivity as the two sets of measurements are made at different temperatures. It has however been established in this laboratory by Douglas (7) that the temperature

(1) Dissertation, Charkow, 1892.

(2) Ztschr. physikal. Chem., 14, 701.

(3) Ibid., 14, 267.

(4) Journ. Phys. Chem., 3, 26.

(5) Ztschr. physikal. Chem., 4, 429.

(6) Ibid., 31, 133.

(7) Dissertation, Johns Hopkins, 1901.

coefficient of dissociation is in aqueous solutions very small if of any value at all, in which case if this holds for alcoholic solutions there should be only a very small difference between the results obtained by the two methods.

Higher Alcohols.: - But very little work has been done on the dissociating power of the higher alcohols. Schlamp (1) has shown from the results of his measurements on solutions of lithium and calcium chlorides, sodium iodide, and lithium salicylate that their conductivity in propyl alcohol is somewhat less than one half that in ethyl alcohol.

In propyl and amyl alcohols Carrara (2) has made a few measurements; while Hartwig (3) determined the conductivity of formic, acetic, and butyric acids in amyl alcohols. Among the iso-alcohols Carrara (4) has worked with isopropyl and Kablukoff (5) with isobutyl and isoamyl showing the remarkable result that in isoamyl alcohol solution the molecular conductivity of hydrochloric acid decreases with increase in dilution. Schall (6) has determined the conductivity of picric acid in isobutyl alcohol.

(1) Ztschr. physikal. Chem., 14, 272.

(2) Gazz. chim. ital., 27, I, 221.

(3) Wied. Ann., 33, 48; 43, 838.

(4) Gazz. chim. ital., 27, I, 221.

(5) Ztschr. physikal. Chem., 4, 432.

(6) Ibid., 14, 707.

Ether. Practically the only work on ethereal solutions is due to Cattaneo (1) and Kablukoff (2). Cattaneo has measured the conductivity of ethereal solutions of cadmium, iodide, cadmium bromide, ferrous and ferric chlorides, aluminium, mercurous, and stannous chlorides, salicylic and hydrochloric acids. He found that ethereal solutions have a negative temperature coefficient of conductivity, and that the molecular conductivity of hydrochloric acid in ether decreased with increase in dilution. This is analogous to the results of Kablukoff in the case of isocaryl alcohol. Indeed Kablukoff found also that the conductivity of hydrochloric acid decreased with the dilution.

Ketones.:- The conductivity of a number of salts of the alkalies in acetone were published by Cattaneo (3) several years ago. About the same time a paper appeared from St.v. Laszcynski (4) on the conductivity of some salts in acetone. Among these were included lithium and mercuric chlorides, potassium iodide, silver nitrate, and potassium, sodium, and ammonium sulphocyanates. The conductivity of solutions in acetone has also been measured by Carrara(5).

(1) Atti R. Acc. delle Scienze, Torino, 28, 329;

Rendic L. Acc. dei Lincei, (5), 2, Isem., 295.

(2) Ztschr. physikal. Chem., 4, 431.

(3) Rend. R.Acc. dei Lincei, (5), 4°, 2 sem., 63-75.

(4) Ztschr. elek. Chem., 1895, 55.

(5) Gazz. chim. ital., 27, I, 207.

Kahlenberg and Lincoln (1) measured the conductivity of solutions of ferric, cupric, and stannous chlorides, and antimony trichloride in acetone; and Dutoit and Aston (2) as well as Dutoit and Friderich, (3) studied a number of solutions in acetone and other Ketones. Dutoit and Aston pointed out as has been mentioned, that those solvents which dissociate to the greatest extent are polymerized as shown by the surface tension method of Ramsay and Shields(4).

In addition to acetone they worked with methyllethylketone and methylpropylketone. In the former solvents they used mercuric chloride, cadmium iodide, ammonium sulphocyanate, and sodium salicylate; in the latter cadmium iodide, ammonium sulphocyanate, and sodium salicylate. They found that in the methyllethylketone the conductivities were larger than in the methylpropylketone, but that the conductivity in acetone was the greatest of the three. Dutoit and Aston conclude from their work, together with that of Kablukoff (5) that there is a general relation between the polymerization of the molecules of a solvent and its dissociating power.

In connection with their work in acetone they make the following remarkable statement; "We have found by the boiling point method that the following salts in acetone have

- (1) Journ. Phys. Chem., 3, 27.
- (2) Compt. Rend., 125, 240.
- (3) Bull. soc. Chim., (3), 19, 321.
- (4) Ztschr. physikal. Chem., 12, 433.
- (5) Ibid.

normal molecular weights: Cadmium iodide, lithium chloride, sodium iodide, mercuric chloride, and ammonium sulphocyanate." and these substances in acetone conduct the current. Some results already obtained in this laboratory seem to throw light on this apparent discrepancy.

Acids. - The dissociating power of formic acid has been quite elaborately investigated by Zanninovich-Tessarin (1). In his work he used mainly the freezing point method but also studied the conductivity of a few salts in this solvent. He measured the freezing point lowerings of formic acid produced by the following substances, at dilutions varying from 0.34 to 3.4 normal (and in some cases at even greater concentration) Potassium, sodium, ammonium, and lithium chlorides; potassium sodium, and ammonium bromides; hydrochloric, acetic, and tri-chloracetic acids. Formic acid is one of the strongest dissociating solvents next to hydrocyanic acid and water. The behavior of hydrochloric acid in this solvent is very remarkable. Not only does it show no dissociation but the molecules are actually polymerized. Although as just mentioned the freezing point lowering showed no dissociation yet the conductivity in this solvent was ver. considerable, This may be due to the fact that while a majority of the molecules were polymerized some were dissociated into ions which carried the current. The conductivities of potassium and sodium chloride in this solvent were also found to be very large.

(1) Ztschr. physikal. Chem., 19, 251.

Zanninovich-Tessarin (1) has also determined the freezing-point lowering produced by sodium bromide and lithium chloride in acetic acid. The former gave normal values, indicating no dissociation, while the latter showed marked polymerization.

The conductivity of sulphuric acid in acetic acid has been measured by Jones (2) who found that the molecular conductivity, which was small at all dilutions increased with the dilution to a certain point and then decreased with further increase in the dilution of the solution. This is somewhat analogous to the results obtained by Kablukoff (3) for hydrochloric acid in ether and in isoamyl alcohol.

The Nitriles and Cyanogen.:- Dutoit and Aston (4) have determined the conductivities of mercuric chloride, sodium bromide, cadmium bromide and iodide, ammonium sulphocyanate, and silver nitrate in propionitrile. The investigation was extended by Dutoit and Friderich(5) to solutions in acetonitrile and butyronitrile. It was shown that the dissociating power is greater in the first members of the nitriles, but in no case do they at all approach the dissociating power of liquid hydrocyanic acid as determined by the recent work of Centnerszwer (6).

Centnerszwer (7) has also shown that liquid cyanogen is a

(1) Ztschr. physikal. Chem., 19, 255.

(2) Am. Chem. Journ., 16, 13.

(4) Compt. Rend., 125, 240.

(5) Bull. soc. chim. (3), 19, 321.

(3) Loc. Cit.

(6) Ztschr. physikal. Chem., 39, 217.

(7) Loc. Cit.

non-dissociant.

Pyridine.:- Werner (1) that certain inorganic salts when dissolved in pyridine conduct the current very well and yet show but very little or no dissociation by the boiling point method. It is however to the work of St.v. Laszczynski and St.v. Gorski (2) that we owe what knowledge we have of the dissociating power of pyridine. They measured the conductivity of lithium chloride, potassium, sodium, and ammonium iodides, and potassium, sodium and ammonium sulphocyanates in pyridine, over a wide range of dilutions.

Other Organic Solvents.:- So very few measurements have been made in other organic solvents that they can be passed over with but the slightest reference. Thus Werner (3) found that cuprous chloride in ethyl sulphide conducts very poorly Cattaneo (4) studied a few solutions in glycerol and found that they had a larger conductivity than the corresponding solutions in ether. They also had larger temperature coefficients of conductivity. Dutoit and Aston (5) measured the conductivities of electrolytes in benzene chloride, ethyl bromide, and amyl acetate and found that these solutions conduct very poorly. They found on the other hand that solutions in nitroethane conduct very well. Dutoit and Friderich (6)

(1) Ztschr. anorg. Chem., 15, I 39.

(2) Ztschr. elek. Chem., 4, 290.

(3) Ztschr. Anorg. Chem., 15, I, 139.

(4) Beibl. Wied. Ann., 17, 365.

(5) Compt. Rend., 125, 240.

(6) Bull. soc. chim., (3), 19, 325.

worked with acetophenone as a solvent, and with cadmium iodide, mercuric chloride, and ammonium sulphocyanate, as electrolytes. The conductivity in this solvent was very small.

Four other solvents have thus far been studied namely ethyl acetate, benzaldehyde, ethyl acetoacetate and nitrobenzene. This work was done by Hahlenberg and Lincoln (1). As electrolytes they use ferric and stannous chlorides bismuth trichloride, and antimony trichloride. The conductivities in these solvents are in general small but vary considerably with the nature of the electrolyte used.

MIXED SOLVENTS.

Hydrogen Dioxide and Water.: - The dielectric constant of a mixture of hydrogen dioxide and water is greater than that of pure water. This has been shown by Calvert (2) and this would lead one to suspect that such mixtures should have a greater conductivity than pure water in accordance with the Nernst Thomson rule. The dissociating power has however not as yet been determined. Reference should also be made to the further work of Calvert (3) showing that hydrogen dioxide has acid properties and to the work of Jones, Barnes and Hyde (4) along the same lines.

(1) Journ. Phys. Chem., 3, 12.

(2) Ann. der Phys., 1, 483.

(3) Ztschr. physikal. Chem., 38, 513.

(4) Am. Chem. Journ., 27, 22.

Mixtures of Water and the Alcohols.:- Nothing but the briefest mention need be made of the work of Jenz, (1) Kerler (2) Stephan, (3) Tablukoff, (4) Carrara, (5) Schall, (6) and Arrhenius. (7) Wakeman (8) in quite an elaborate investigation, measured the conductivity of organic acids in mixtures of ethyl alcohol and water containing varying amounts of alcohol. The results showed that the conductivity became gradually smaller as the amount of alcohol became larger and larger. This is just what would be expected from the relative conductivities in these two solvents.

Zelinsky and Yraiwin (9) have however obtained results of a very different character. They found that the salts with which they worked when dissolved in a mixture of methyl alcohol and water containing 50 per cent methyl alcohol and 50 per cent water, gave a conductivity considerably less than the conductivity in either alcohol or water.

- (1) Mem. de l'Acad. de St. Petersbourg, (7), 30, 1881.
- (2) Dissertation, (Erlangen), 1884.
- (3) Wied. Ann., 17, 675.
- (4) Ztschr. physikal. Chem., 4, 432.
- (5) Gazz. chim. ital., 16, 1.
- (6) Ztschr. physikal. Chem., 14, 701.
- (7) Ibid., 9, 487.
- (8) Ibid., 11, 49.
- (9) Ibid., 21, 35.

Similar results have been obtained by Cohen (1) with ethyl alcohol and water, but only when the mixture contained very little water and at dilutions which were quite large, as is shown by the following table.

Potassium Iodide.

Pure alcohol	80 parts alcohol and 20 parts water.	
v.	v18°	v18°
64	26.1	30.9
128	29.2	32.2
256	31.8	33.2
512	34.4	34.1
1024	36.0	34.5
2048	36.3	35.0

From a study of the above results it is seen that the conductivities in the mixtures of water and alcohol are the greater till a dilution of 512 litres is reached, when the conductivity in the pure alcohol becomes greater than that of the alcohol containing 20 per cent of water.

In general however Cohen found that addition of water increased the conductivity as we would expect.

(1) Ztschr. physikal. Chem., 25, 31.

Part II. Experimental.

Introduction.

This work was undertaken as a continuation of the older work of Zelinsky and Krapiwin (1) and Cohen (2) on the conductivity of electrolytes in mixtures of methyl and ethyl alcohol with water. Zelinsky and Krapiwin in their work have shown that solutions in a fifty per cent mixture of methyl alcohol and water have a much less conductivity than in the pure alcohol itself. They have also shown that the slightest addition of water to a solution of an electrolyte in absolute methyl alcohol produced a lowering of its conducting power.

I have extended this work by making conductivity measurements of solutions in which the solvents have been mixtures of methyl alcohol and water of varying composition. By this means I have been able to plot curves showing ~~the~~ for each salt with which I have worked, the mixture of methyl alcohol and water having the least dissociating power.

I have also worked with ethyl alcohol, propyl alcohol, and with mixtures of ethyl alcohol and water, propyl alcohol and water, and of methyl alcohol and ethyl alcohol.

The work has for the most part been done both at 0° and 25°. In this way I have been able to calculate the temperature coefficients of conductivity of the various salts in the different solvents, and what is of more importance to

(1) Loc. Cit.

(2) Loc. Cit.

show the influence of temperature on the minimum values mentioned above.

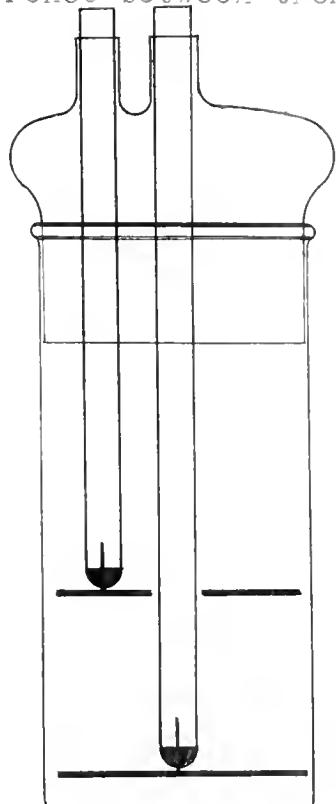
are

The salts used ~~have been~~ potassium iodide, strontium iodide, ammonium bromide, cadmium bromide, ferric chloride, and lithium nitrate.

Apparatus.

In all these measurements the Kohlrausch method of measuring conductivity was employed. The bridge wire used was a metre in length and of "manganin". The resistance coils were manufactured by Leeds and Co., Philadelphia, and were guaranteed accurate to $1/25$ of 1 per cent.

The cells used were all of the following form. The difference between them and the ordinary Arrhenius cell being



that these were provided with a ground glass top to prevent evaporation of the more volatile solvents, and to protect the anhydrous alcohols from the moisture of the baths and air. In some cases the ground glass joint was also paraffined as an extra precaution.

The zero bath was prepared as follows. A large glass battery jar was filled with pure well crushed ice and moistened with distilled water. This was placed in a water bath the space between the two being filled with well crushed ice.



By this means it is possible to keep a cell within 0.02° of zero for hours. The 25° bath was of the ordinary form and was stirred by means of a small hot air engine.

The thermometers used were graduated to 1/25 th of a degree and were carefully standardized. The burettes and flasks had also been carefully calibrated.

Solvents.

Water:- All the water used in this work was purified as follows: Ordinary distilled water was first distilled from potassium bichromate. This water was, when wanted, redistilled from potassium bichromate acidified with sulphuric acid and then from barium hydroxide. The water purified in this way had a conductivity of never more than 2×10^{-6} and sometimes went as low as 0.8×10^{-6}

Methyl Alcohol:- The methyl alcohol used was the best obtainable commercial article. It was first boiled with calcium oxide, then distilled and allowed to stand over anhydrous copper sulphate for weeks. Before use it was distilled from the copper sulphate and then from sodium. None of the alcohol used in making up the absolute alcohol solutions had been distilled from sodium more than twenty-four hours before use. It had a conductivity of 2.3×10^{-6}

Ethyl Alcohol:- The ethyl alcohol was the best obtainable article and was purified just as the methyl alcohol. Its conductivity had a mean value of 2.1×10^{-7}

Propyl Alcohol:- The propyl alcohol was Kahlbaum's best and before use was distilled from anhydrous copper sulphate

and sodium. It had a conductivity of about 2.8×10^{-7}

Solutions.

The method of making up the original mother solutions will be given in the consideration of the various electrolytes

From this mother solution the remainder were made by successive dilutions by means of burettes and flasks. In the cases where this would necessitate the use of small quantities of the solution a second mother solution was made and from this successive dilutions were prepared.

In making the solutions in the mixed solvents a sufficient quantity of this solvent was made by mixing the constituents in the required proportions. This was then used in the same manner as a simple solvent.

In preparing these mixed solvents the following method was used. "x" cubic centimetres of an alcohol was diluted to 100 cubic centimetres. In the following; such a solution would be designated as - alcohol x per cent. In making mixtures of methyl alcohol and ethyl alcohol the methyl alcohol was measured and diluted with the ethyl alcohol and the concentration expressed in terms of the methyl alcohol

Conductivity Measurements.

In all determinations of conductivity, from three to five different resistances were used and the values given in the tables are the mean value of these.

POTASSIUM IODIDE.

The salt used in this work was carefully recrystallized a number of times. It was then carefully dried and kept in a desiccator. All the mother solutions were made by direct weighing.

Table I. Molecular Conductivity of Potassium Iodide
in Water.

Potassium iodide, KI. Molec. wt., 166.00.

v.	$\mu_v^{0^\circ}$	$\mu_v^{25^\circ}$
64	74.09	132.1
128	76.4 D	135.4
256	77.01	138.0
512	78.0 D	139.6
1024	77.96	140.7

The values of the conductivity at 0° marked "D" are due to Douglas (1), while those at 25° are all taken from the work of Ostwald.

Table II. Molecular Conductivity of Potassium Iodide
in Ethyl Alcohol.

v.	$\mu_v^{0^\circ}$	$\mu_v^{25^\circ}$
64	19.12	29.40
128	21.36	33.02
256	22.66	36.02
512	25.00	38.63
1024	27.45	41.35

(1) Dissertation, Johns Hopkins, 1901.

Table III. Molecular Conductivity of Potassium Iodide
in Methyl Alcohol.

v.	μ_{v0°	μ_{v25°
64	59.32	82.87
128	63.88	88.49
256	67.73	93.73
512	69.85	98.36
1024	71.23	102.0

The conductivity of solutions of potassium iodide in methyl alcohol had already been determined by both Zelinsky and Krapiwin (1) and Carrara (2), but with such different results that the above measurements seemed necessary. My measurements agreed very well with those of Zelinsky and Krapiwin as is seen from the following table.

Table IV. Molecular Conductivity of Potassium Iodide
in Methyl Alcohol

v.	μ_{v25° Carrara	μ_{v25° Zelinsky & Krapiwin.
64	78.7	82.52
128	84.7	88.69
256	88.2	93.85
512	90.8	98.19
1024	93.0	102.2

(1) Ztschr. physikal. Chem., 21, 35.

(2) Gazz. chim. ital., 26 (1), 119.

Table V. Molecular Conductivity of Potassium Iodide
in Methyl Alcohol (20 per cent.) and Water.

v.	μ_{v0°	μ_{v25°
64	45.69	91.91
128	47.26	93.78
256	47.79	95.64
512	48.45	97.12
1024	49.07	98.10

Table VI. Molecular Conductivity of Potassium Iodide
in Methyl Alcohol (40 per cent.) and Water.

v.	μ_{v0°	μ_{v25°
64	35.48	72.14
128	35.92	73.62
256	36.52	75.14
512	37.02	76.25
1024	37.85	77.62

Table VII. Molecular Conductivity of Potassium Iodide
in Methyl Alcohol (50 per cent.) and Water.

v.	μ_{v0°	μ_{v25°
64	33.73	67.46
128	34.44	68.79
256	35.13	70.37
512	36.05	71.72
1024	36.76	72.57

Table VIII. Molecular Conductivity of Potassium Iodide
in Methyl Alcohol (65 per cent.) and Water.

v.	μ_{v0°	μ_{v25°
64	35.12	65.04
128	35.71	67.25
256	36.49	68.75
512	37.23	70.00
1024	37.75	70.94

Table IX. Molecular Conductivity of Potassium Iodide
in Methyl Alcohol (80 per cent.) and Water.

v.	μ_{v0°	μ_{v25°
64	39.03	67.75
128	40.51	70.35
256	41.83	71.85
512	43.23	73.15
1024	44.45	74.81

Table X. Molecular Conductivity of Potassium Iodide
in Ethyl Alcohol (50 per cent.) and Water.

v	μ_{v0°	μ_{v25°
64	19.26	48.30
128	19.82	50.07
256	20.35	50.80
512	20.92	51.97
1024	21.43	52.52

Table XI. Molecular Conductivity of Potassium Iodide
Methyl Alcohol (50 per cent) and ethyl
Alcohol

v.	v ^{0°}	v ^{25°}
64	36.74	54.18
128	39.46	58.52
256	41.93	62.13
512	44.46	65.93
1024	46.89	69.61

Table XII. Temperature coefficients of Conductivity
of Potassium Iodide in Water (0°-25°).

v.	
64	2.26
128	2.30
256	2.35
512	2.40
1024	2.52

Table XIII. Temperature Coefficients of Conductivity
of Potassium Iodide in Methyl Alcohol

0°-25°

v.	
64	0.942
128	0.984
256	1.04
512	1.14
1024	1.23

Table XIV. Temperature Coefficients of Conductivity
of Potassium Iodide in Ethyl Alcohol
0°-25°.

v.	
64	0.411
128	0.466
256	0.534
512	0.545
1024	0.557

Table XV. Temperature Coefficients of Conductivity
of Potassium Iodide in Mixtures of Methyl
Alcohol and Water of Various Compositions.

v.	20	40%	50%	65%	80%
64	1.85	1.47	1.35	1.17	1.15
128	1.86	1.51	1.37	1.26	1.17
256	1.91	1.54	1.41	1.29	1.20
512	1.95	1.57	1.43	1.31	1.20
1024	1.96	1.59	1.43	1.32	1.21

Table XVI. Temperarure Coefficients of Conductivity
of Potassium Iodide in a Mixture of Ethyl
Alcohol and Water (50 per cent)

v.	0°-25°
64	1.16
128	1.25
256	1.22
512	1.24
1024	1.24

Table XVII. Temperature Coefficient of Conductivity
of Potassium Iodide in a Mixture of
Methyl and Ethyl Alcohols (50 per cent)

v.	0°-25°
64	0.698
128	0.762
256	0.808
512	0.859
1024	0.909

In order that one may be able to see the connection existing between the conducting power of the solutions in the various solvents, I give the following tables of comparison.

Table XVIII. Comparison of the Molecular Conductivity of
Potassium Iodide in Water, Methyl Alcohol, and
Mixtures of these Solvents at 0°.

v.	0%	20%	40%	50%	65%	80%	100%
64	74.09	15.69	35.48	33.73	35.12	39.03	59.32
128	76.4 D	47.26	35.92	34.44	35.71	40.51	63.88
256	77.01	47.79	36.52	35.13	36.49	41.83	67.73
512	78.0 D	48.45	37.02	36.05	37.23	43.23	69.85
1024	77.96	49.07	37.85	36.76	37.75	44.45	71.23

The values in this table have been plotted on Plate I. It is seen that the values of the molecular conductivity reach a minimum in a mixture of methyl alcohol and water containing 50 per cent methyl alcohol.

It is also seen that an addition of approximately 10 per cent of alcohol lowers the conductivity of the water solutions to that of an alcohol solution.

Plate I

Curves
Showing Relation
between
Conductivity
of
Solutions
of
Potassium Iodide
in
Water, Methyl
Alcohol,
and
Mixture
at 0°C

Curve I Dilution = 64
" II " = 128
" III " = 256
" IV " = 512
" V " = 1024

Molecular Conductivity

40

60

I

70

50

40

30

20

10

V

IV

III

II

I

Strength of Alcohol



30 0%^o

20 0%^o

40 0%^o

60 0%^o

80 0%^o

100 0%^o

Table XIX. Comparison of the Molecular Conductivity of Potassium Iodide in Water, Methyl Alcohol, and Mixtures of these Solvents. at 25°.

v.	0%	20%	40%	50%	65,	80%	100%
64	132.1	91.91	72.14	67.46	65.04	67.78	82.87
128	135.4	93.78	73.69	66.79	67.25	70.33	88.49
256	138.0	95.64	75.14	70.37	68.78	71.83	93.73
512	139.6	97.12	76.25	71.72	70.00	73.16	98.36
1024	140.7	98.10	77. <u>6</u> 8	72.57	70.94	74.81	102.0

The results given in this table are plotted on Plate II.

The curve is of the same general form as the preceding one. The chief points of difference are:— The minimum point has shifted to the right corresponding now for an alcohol-water mixture of about 65 per cent. The increase to the right of the minimum is much less rapid than that to the left, the difference being due to the fact that the temperature coefficient of conductivity is much greater in water than in methyl alcohol. The alcohol-water mixture having the same conducting power as pure methyl alcohol solution has also changed. In this case it changes from an alcohol of about 19 per cent to an alcohol of about 30 per cent, depending on the concentration of the solution.

Plate II

Curves
Showing Relation
between
Conductivity
of
Solutions
of
Potassium Iodide
in
Water, Methyl Alcohol
and
Mixture
at
 25°C

Curve I, Dilution = 64
 " II " = 128
 " III " = 256
 " IV " = 512
 " V " = 1024

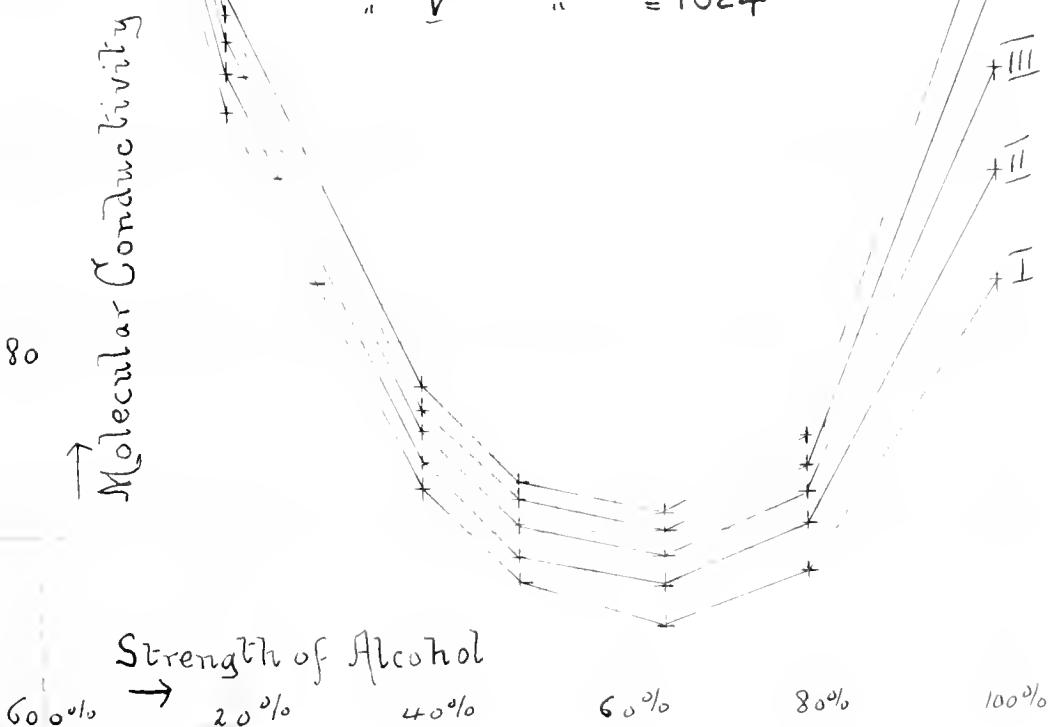


Table XX. Comparison of the Molecular Conductivity of Potassium Iodide in Ethyl Alcohol, Water, and a Mixture of these (50 per cent).

v.	0°		
	μ_v Water.	μ_v Mixture	$\frac{\mu_v}{\text{Ethyl}}_{\text{Alcohol.}}$
64	74.09	19.26	19.12
128	76.4	19.82	21.36
256	77.01	20.35	21.66
512	78.0	20.92	25.00
1024	77.96	21.43	27.43

Table XXI. Comparison of the Molecular Conductivity of Potassium Iodide in Ethyl Alcohol, Water, and a Mixture of these (50 per cent).

v.	25°		
	μ_v Water	μ_v Mixture.	$\frac{\mu_v}{\text{Ethyl}}_{\text{Alcohol}}$
64	132.1	48.30	29.40
128	135.4	50.07	33.02
256	138.0	50.80	36.02
512	139.6	51.97	38.63
1024	140.7	52.52	41.35

Cohen (1) has shown that solutions of potassium iodide in a mixture of alcohol and water show a minimum in the conductivity, but only at great dilutions (512) and when the amount of water present is small. His work was however all done at 18°C. From the results in Table XX however we see

(1) Loc. Cit.

that at 0° we have a minimum in the conductivity values for an alcohol as dilute as 50 per cent and in solutions comparatively strong, namely from v=128 on. In all probability in alcohol of 75 to 80 per cent a much greater depression will be found. This is however subject for future investigation. At 25° all trace of a minimum has disappeared.

Table XXII. Comparison of the Molecular Conductivity of Potassium Iodide in Methyl Alcohol, Ethyl Alcohol, and a Mixture of these (50 per cent).

0°			
v.	$\frac{\mu}{v}$ Methyl Alcohol	$\frac{\mu}{v}$ Mixture.	$\frac{\mu}{v}$ Ethyl Alcohol
64	59.32	36.74	19.12
128	63.88	39.46	21.36
256	67.75	41.93	22.66
512	69.85	44.46	25.00
1024	71.25	46.89	27.43

Table XXIII. Comparison of the Molecular Conductivity of Potassium Iodide in Methyl Alcohol, Ethyl Alcohol, and a Mixture of these (50 per cent) at 25°

v.	Methyl	Mixture.	Ethyl
	Alcohol	v	Alcohol
64	82.87	54.18	29.40
128	88.49	56.57	33.02
256	93.75	62.13	37.02
512	98.36	65.93	38.63
1024	102.0	69.61	41.35

These last two tables make it clear that in a mixture of methyl and ethyl alcohols the conductivity of potassium iodide shows no minimum value when compared with the conductivity in the pure solvents. In fact the conductivity values for the solutions in the mixed solvent approach the mean values of the conductivities in the pure solvents. Thus at 0° the observed value of the conductivity, in the mixture, for V=64 is 36.74 while the mean of the conductivities at the same dilution in the pure solvents is 39.2. In all cases however, the conductivity in the mixture lies below this mean value.

AMMONIUM BROMIDE.

The salt used in this work was all carefully crystallized and on sublimation left no residue. It was thoroughly dried and kept in a desiccator. All the mother solutions were made by direct weighing.

Table XXIV. Molecular Conductivity of Ammonium Bromide in Water.

Ammonium Bromide, NH_4Br , Molec. Wt., 98.04.

v.	μ_{v0°	μ_{v25°
64	74.32	135.3 (Z.&K.)
128	75.23	138.6
256	76.62	141.2
512	77.49	143.5
1024	77.78	145.6

Table XXV. Molecular Conductivity of Ammonium Bromide in Methyl Alcohol.

v.	μ_{v0°	μ_{v25°
64	58.71	79.56 (Z.&K.)
128	63.16	85.30
256	66.45	90.38
512	68.51	94.99
1024	70.40	98.24

The values at 25° are all taken from the work of Zelinsky and Krapivin.

Table XXVI. Molecular Conductivity of Ammonium Bromide
in Ethyl Alcohol.

v.	μ_{v0°
64	16.71
128	18.83
256	19.66
512	22.6
1024	22.88

Table XXVII. Molecular Conductivity of Ammonium Bromide
in Methyl Alcohol (50 per cent) and water.

v.	μ_{v0°
64	34.85
128	35.78
256	36.36
512	37.11
1024	37.49

Table XXVIII. Molecular Conductivity of Ammonium Bromide
in Ethyl Alcohol (50 per cent) and Water.

v.	μ_{v0°
64	19.42
128	19.89
256	20.09
512	20.70
1024	21.50

Table XXIX. Molecular Conductivity of Ammonium Bromide in Methyl Alcohol, (50 per cent) and Ethyl Alcohol.

v.	v ⁰
64	34.15
128	38.40
256	39.75
512	41.06
1024	42.00

Table XXX. Temperature Coefficient of Conductivity of Ammonium Bromide in Water.

v.	0°-25°
64	2.44
128	2.54
256	2.56
512	2.64
1024	2.71

Table XXI. Temperature Coefficient of Conductivity of Ammonium Bromide in Methyl Alcohol.

v.	0°-25°
64	0.834
128	0.906
256	0.977
512	1.059
1024	1.114

Table XXXII. Comparison of the Molecular Conductivity
of Ammonium Bromide in Water, Methyl Alcohol,
and a Mixture of these (50 per cent) at 0°.

v.	Water.	Mixture.	Methyl Alcohol
v.	v0°	v0°	v0°
64	74.32	34.85	58.71
128	75.23	35.78	63.16
256	76.62	36.36	66.45
512	77.49	37.11	68.51
1024	77.78	37.49	70.40

Table XXXIII. Molecular Conductivity of Ammonium Bromide
(V=64) In Methyl Alcohol, Water and Mixtures
of these at 0°.

Alcohol in per cent.	μ_{v0°
0	74.22
20	47.96
50	34.85
65	34.68
80	40.55
100	58.71

We see that in these results we have practically the same phenomenon as in the case of potassium iodide. In the case of ammonium bromide the minimum point in the conductivity values appears to be reached with an alcohol of 50 per cent.

Table XXXIV. Comparison of the Molecular Conductivity of Ammonium Bromide in Water, Ethyl Alcohol, and a Mixture (50 per cent) of these at 0°.

v.	Water.	Mixture.	Ethyl Alcohol.
	μ_{v0°	μ_{v0°	μ_{v0°
64	74.22	19.42	16.71
128	75.23	19.89	18.83
256	76.62	20.09	19.66
512	77.49	20.70	22.66
1024	77.78	21.50	22.88

From this table we see that here also a 50 per cent ethyl alcohol gives a minimum but only in the case of the more dilute solutions, namely for dilutions $v = 512$ and 1024 .

Table XXXV. Comparison of the Molecular Conductivity of Ammonium Bromide in Methyl Alcohol, Ethyl Alcohol, and a Mixture of these (50 per cent). at 0°.

v.	Methyl Alcohol.	Mixture.	Ethyl Alcohol
	μ_{v0°	μ_{v0°	μ_{v0°
64	58.71	34.15	16.71
128	63.16	38.40	18.83
256	66.45	39.75	19.66
512	68.51	41.06	22.66
1024	70.40	42.00	22.88

In this comparison there is no trace of a minimum, nor does there appear to be the slightest chance of there being one, for any mixture of methyl and ethyl alcohols.

STRONTIUM IODIDE.

The strontium iodide used in this work was a sample of Bender and Hobein's best material. It was practically free from impurities. The material was dried as follows: It was carefully heated with a little ammonium iodide in a current of pure dry hydrogen till all the water and ammonium iodide was driven off. After cooling in the hydrogen stream it was at once dissolved. The solutions were perfectly neutral and showed not the slightest coloration with starch solution. No trace of ammonium salts could be detected.

Table XXXVI. Molecular Conductivity of Strontium Iodide
in Water.

Strontium Iodide, SrI₂, Molec. Wt. 341.3

v.	μ_{v0°	μ_{v25°
32	113.1	205.3
64	117.7	214.5
128	122.1	223.1
256	126.0	231.8
512	129.8	240.2
1024	132.6	245.9

Table XXXVII. Molecular Conductivity of Strontium Iodide
in Methyl Alcohol.

v.	μ_{v0°	μ_{v25°
32	75.82	101.4
64	85.01	115.3
128	94.76	128.6
256	104.4	141.4
512	114.0	153.9
1024	123.4	161.3

Table XXXVIII. Molecular Conductivity of Strontium Iodide
in Ethyl Alcohol.

v.	μ_{v0°	μ_{v25°
32	17.44	24.00
64	20.28	28.58
128	25.66	33.53
256	27.00	38.88
512	32.07	46.13
1024	36.01	51.25

Table XXXIX. Molecular Conductivity of Strontium Iodide
in Propyl Alcohol.

v.	μ_{v0°	μ_{v25°
32	4.70	7.58
64	5.62	8.84
128	6.52	10.20
256	7.41	11.32

Table XL. Molecular Conductivity of Strontium Iodide
in Methyl Alcohol (25 per cent) and Water.

v.	μ_{v0°	μ_{v25°
32	65.06	131.3
64	66.05	138.5
128	68.62	145.3
256	70.98	152.3
512	73.10	157.4
1024	75.51	161.9

Table XLI. Molecular Conductivity of Strontium Iodide
in Methyl Alcohol (50 per cent) and Water.

v.	μ_{v0°	μ_{v25°
32	50.19	103.8
64	52.61	109.9
128	55.05	115.3
256	57.13	120.1
512	59.51	124.3
1024	61.03	128.5

Table XLII. Molecular Conductivity of Strontium Iodide
in Methyl Alcohol (75 per cent) and Water.

v.	μ_{v0°	μ_{v25°
32	55.53	98.09
64	59.24	104.8
128	62.85	111.4
256	66.68	118.0
512	69.98	124.8
1024	73.22	131.4

Table XLIII. Molecular Conductivity of Strontium Iodide
in Ethyl Alcohol (50 per cent) and Water.

v.	μ_{v0°	μ_{v25°
32	28.32	72.51
64	29.72	76.89
128	31.25	80.21
256	32.23	83.21
512	33.22	86.44
1024	34.16	89.32

Table XLIV. Molecular Conductivity of Strontium Iodide in Propyl Alcohol (50 per cent) and Water.

v.	μ_{v0°	μ_{v25°
32	27.40	67.67
64	28.63	71.63
128	29.83	75.44
256	30.98	79.32

Table XLV. Temperature Coefficient of Conductivity of Strontium Iodide in Water.

v.	$0^\circ - 25^\circ$
32	3.29
64	3.87
128	4.04
256	4.23
512	4.42
1024	4.53

Table XLVI. Temperature Coefficient of Conductivity of Strontium Iodide in Methyl Alcohol.

v.	$0^\circ - 25^\circ$
32	1.02
64	1.21
128	1.35
256	1.48
512	1.60
1024	1.72

Table XLVI. Temperature Coefficient of Conductivity of
Strontium Iodide in Ethyl Alcohol

v.	0°-25°
32	0.262
64	0.344
128	0.396
256	0.475
512	0.562
1024	0.610

Table XLVIII. Temperature Coefficient of Conductivity of
Strontium Iodide in Propyl Alcohol.

v.	0°-25°
32	0.115
64	0.129
128	0.147
256	0.156

Table XLIX. Temperature Coefficient of Conductivity of
Strontium Iodide in Various Mixtures of
Methyl Alcohol and Water.

v.	25%	50%	75%
32	2.73	2.14	1.70
64	2.90	2.9	1.8
128	3.07	2.41	1.94
256	3.25	2.52	2.05
512	3.37	2.59	2.19
1024	3.45	2.70	2.33

Table L. Temperature Coefficient of Conductivity of
Strontium Iodide in Ethyl Alcohol (50 per cent)
and Water.

v.	0°-25°
32	1.77
64	1.89
128	1.96
256	2.04
512	2.13
1024	2.21

Table LI. Temperature Coefficient of Conductivity of
Strontium Iodide in Propyl Alcohol (50 per cent)
and Water.

v.	0°-25°
32	1.61
64	1.72
128	1.82
256	1.93

Table LII. Comparison of the Molecular Conductivity of
Strontium Iodide in Water, Methyl Alcohol,
and Mixtures of these Solvents at 0°.

v.	0%	25%	50%	75%	100%
32	113.1	63.06	50.19	55.55	75.82
64	117.7	66.05	52.61	59.24	85.01
128	122.1	68.62	55.05	62.85	94.76
256	126.0	70.98	57.18	66.68	104.4
512	129.3	73.10	59.51	69.97	114.0
1024	132.6	75.51	61.03	75.22	125.4

Plate III

Curves
Showing Relation
between
Conductivity
of
Solutions
of

Strontium Iodide

Water, Methyl Alcohol
and
Mixture

at
 0°C

Curve I. $V = 32$
II. $V = 64$
III. $V = 128$
IV. $V = 256$
V. $V = 512$
VI. $V = 1024$

→
Concentration
of
Alcohol

0%

25

50

75

100

The results of Table LII. are plotted as Plate III. It is seen that the curve is of identically the same form as for potassium iodide at the same temperature. The minimum point is reached with an alcohol of about 50 per cent.

Table LIII. Comparison of the Molecular Conductivity of
Strontium Iodide in Water, Methyl Alcohol,
Mixtures of these Solvents at 25°.

v.	0%	25%	50%	75%	100%
32	205.3	131.3	103.8	98.09	101.4
64	214.5	138.5	109.9	104.8	115.3
128	223.1	145.3	115.3	111.4	128.6
256	231.9	152.5	120.1	116.0	141.4
512	240.2	157.4	124.3	124.8	153.9
1024	245.9	161.9	128.5	131.4	166.3

The results of this table are plotted as Plate IV. It is seen that in this curve the effect of temperature has been such as to almost completely blot out the minimum value in the curve for V=32 and in the other cases the minimum is much less pronounced than in the curves thus far studied. The effect of temperature is also to shift the minimum point to the right, the minimum point being for an alcohol of about 65-70 per cent.

Plate IV

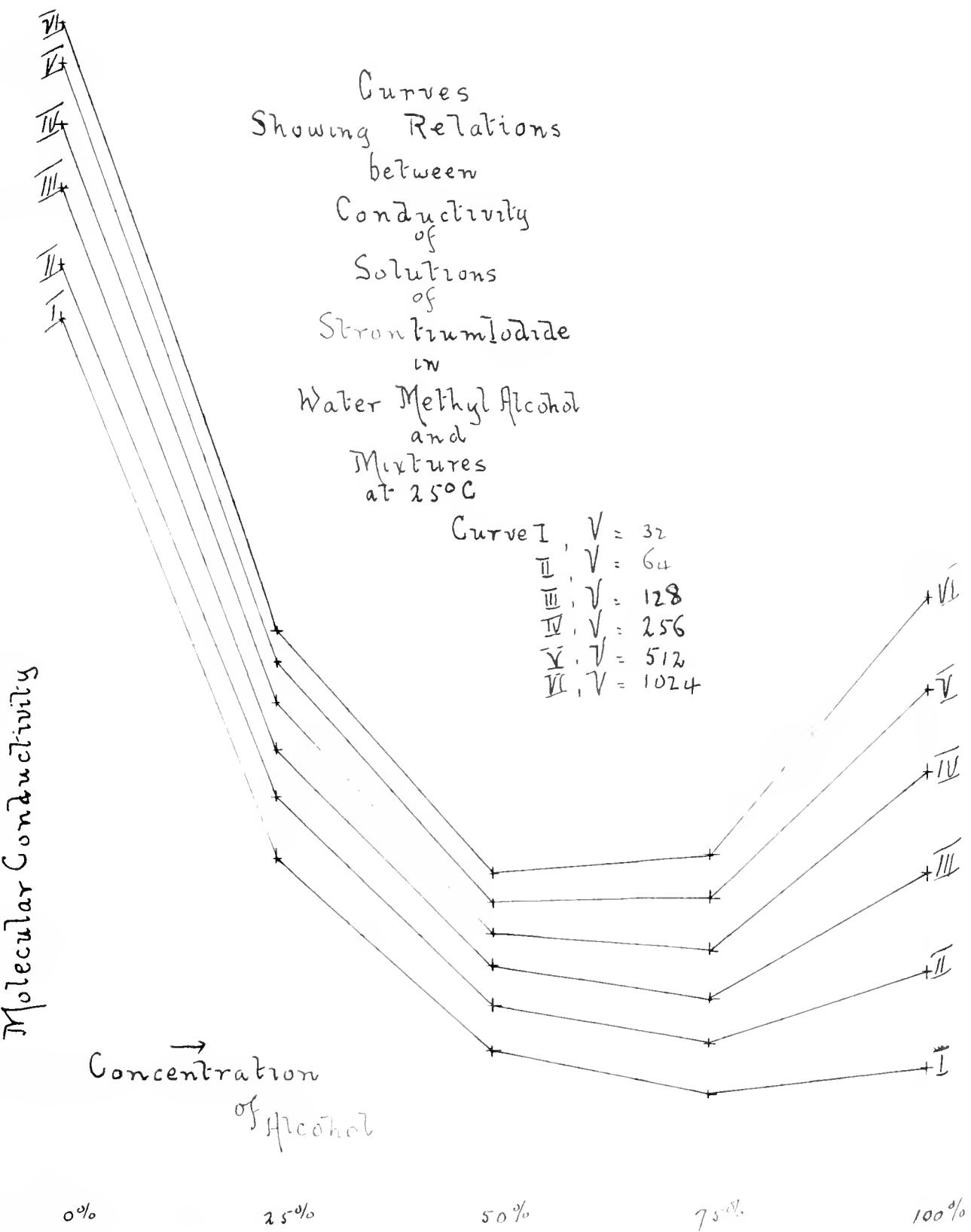


Table LIV. Comparison of the Molecular Conductivity of
Strontium Iodide in Water, Ethyl Alcohol, and
a Mixture of these (50 per cent).

v.	0°		
	μ_v Water.	μ_v Mixture.	μ_v Ethyl Alcohol.
32	115.1	28.32	17.44
64	117.7	29.72	20.28
128	122.1	31.25	23.66
256	126.0	32.23	27.00
512	129.8	33.21	32.07
1024	132.6	34.16	36.01
25°			
32	205.3	72.51	54.00
64	214.5	76.83	58.88
128	223.1	80.21	63.13
256	231.8	83.21	68.88
512	240.2	86.4	73.13
1024	248.9	89.32	71.25

In the table for 0° we see that the values for pure ethyl alcohol are in the stronger solutions much smaller than those for the mixture. They however increase more rapidly and in the most dilute solutions pass the values for the mixture giving us again the minimum point. At 25° there is not the slightest trace of a minimum point although the values are well below the mean of the values for the pure solvents.

In comparing the values for a mixture of propyl alcohol and water with those for the pure solvents, we find that there is not the slightest trace of a minimum at either 0° or 25°.

CADMIUM IODIDE.

The cadmium iodide which was used was a sample which had been used in some previous work in this laboratory, and had been then very carefully purified. The solutions were made by direct weighing.

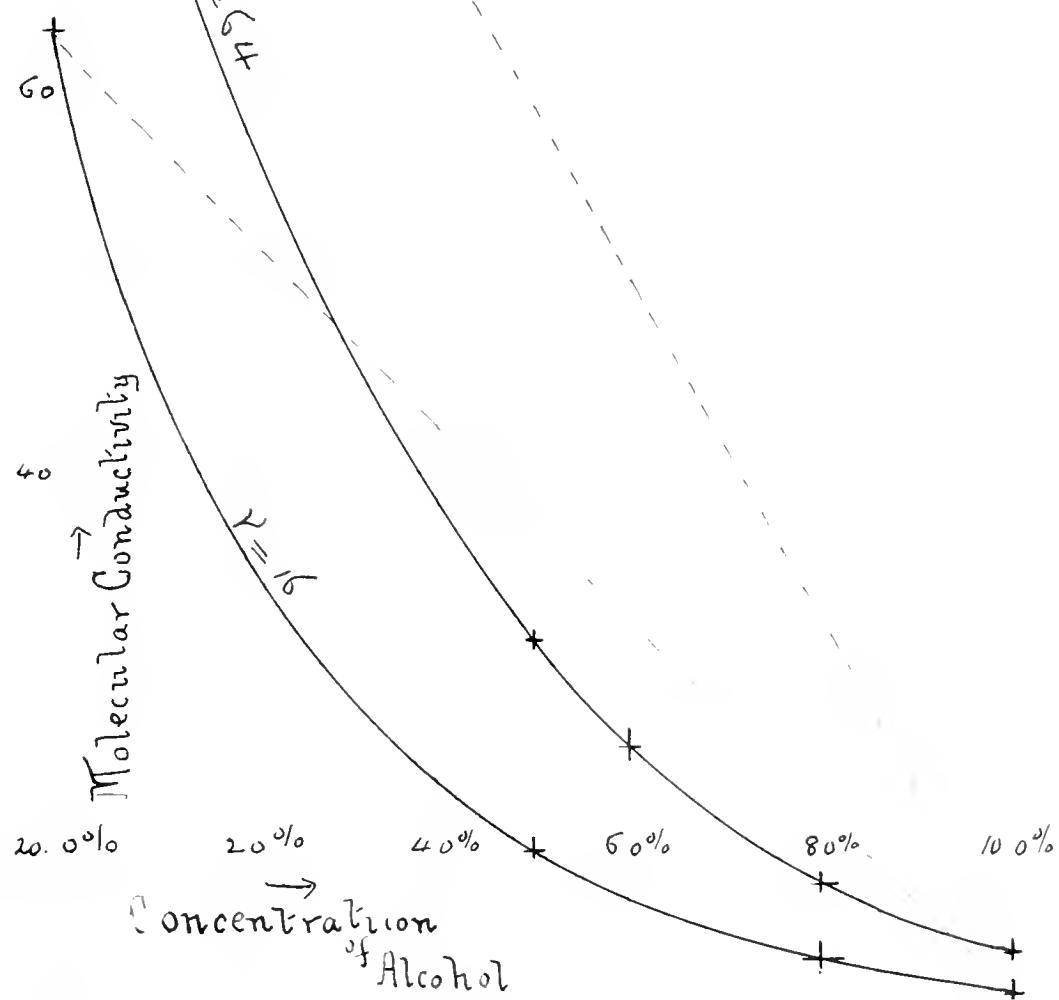
Table LV. Comparison of the Molecular Conductivity of Cadmium Iodide in Methyl Alcohol, Water, and a Mixture (50 per cent) of these at 25° C.

v.	Water. μ_v	Mixture. μ_v	Methyl Alcohol. μ_v
16	62.98	20.31	13.07
32	81.96	24.22	13.59
64	104.7	31.17	14.11
128	129.3	42.03	14.78
256	153.6	50.43	15.44
Concentration of Alcohol.	V=16 μ_v	V=64 μ_v	
0%	62.98	104.7	
50		20.31	31.17
60			25.66
80		14.70	18.41
100		15.07	14.16

When the results in the second part of this table are plotted no trace of a minimum appears. (Plate V.) A considerable difference is however noticed between the values obtained and that required from the law of mixtures, the conductivity values obtained being always lower.

Plate V

Curves
Showing Relation
between
Solutions
of
Cadmium Iodide
in
Various Mixtures
of
Methyl Alcohol
and
Water



LITHIUM NITRATE.

The lithium nitrate used in this work was a sample obtained guaranteed chemically pure by Kalibaum. It was dried in an air bath at 150° and kept in a desiccator. The solutions were made by direct weighing.

Table LVI. Molecular Conductivity of Lithium Nitrate in Water.

Lithium Nitrate, $TiNO_3$, elec. wt., 69.0

v.	μ_{v0°	μ_{v25°	μ_{v25° (Ostwald)
32	50.00	91.53	91.0
64	51.49	94.71	94.5
128	52.51	98.00	97.7
256	53.40	99.6	100.0
512	54.70	101.3	101.0
1024	55.30	102.3	102.0

Table LVII. Molecular Conductivity of Lithium Nitrate in Methyl Alcohol.

v.	μ_{v0°	μ_{v25°
32	45.97	63.51
64	40.12	69.32
128	53.95	74.51
256	56.67	80.57
512	60.06	83.31
1024	63.40	81.4

From these two tables we see that at 0° the conductivity in pure methyl alcohol although starting lower than the conductivity in water increases more rapidly so that we have solutions in methyl alcohol with greater conductivity than

solutions of the same strength in water. This is as far as I know the first instance of such a phenomenon. That my measurements are accurate is shown by the close agreement with Ostwald's values. The solutions measured at 0° were the same as at 25°. The conductivity of a number of the solutions in methyl alcohol were retaken using a different sample of alcohol and salt. In all cases the agreement was all that could be desired.

Table LVIII. Molecular Conductivity of Lithium Nitrate in Ethyl Alcohol.

v.	$\mu_v 0^\circ$	$\mu_v 25^\circ$
32	14.29	21.99
64	15.60	24.85
128	17.52	27.72
256	19.39	30.61
512	21.36	33.25
1024	23.29	35.51

Table LIY. Molecular Conductivity of Lithium Nitrate in Ethyl Alcohol (50 per cent) and Water.

v.	$\mu_v 0^\circ$	$\mu_v 25^\circ$
32	13.10	33.73
64	13.56	35.57
128	14.27	37.08
256	14.63	38.85
512	15.45	40.14
1024	16.16	41.35

From tables LVIII and LIX it is seen that with lithium nitrate a minimum point is found in the conductivity values at 0° and through all the dilutions worked with. At 25° no trace of minimum values are apparent.

Table LX. Molecular Conductivity of Lithium Nitrate in Methyl Alcohol (5 per cent) and Water.

v	μ_{v0°	μ_{v25°
32	29.15	60.56
64	29.68	62.16
128	30.16	63.77
256	30.70	64.96
512	31.35	66.78
1024	32.56	69.02

Table LXI. Molecular Conductivity of Lithium Nitrate in Methyl Alcohol (50 per cent) and Water.

v	μ_{v0°	μ_{v25°
32	23.59	47.67
64	24.49	49.82
128	25.03	51.50
256	25.71	53.57
512	26.35	54.62
1024	27.55	55.60

Table LXII. Molecular Conductivity of Lithium Nitrate
in Methyl Alcohol (75 per cent) and Water.

v.	μ_v 0°	μ_v 25°
32	26.67	47.06
64	27.95	49.52
128	28.66	51.64
256	29.51	54.36
512	30.64	56.68
1024	31.31	57.56

Table LXIII. Temperature Coefficients of Conductivity of
Lithium Nitrate in Water.

v.	0°-25°
32	1.67
64	1.72
128	1.82
256	1.85
512	1.86
1024	1.88

Table LXIV. Temperature Coefficient of Conductivity of
Lithium Nitrate in Methyl Alcohol.

v.	0°-25°
32	0.702
64	0.765
128	0.822
256	0.956
512	0.930
1024	0.922

Table LXV. Temperature Coefficients of Conductivity of
Lithium Nitrate in Ethyl Alcohol.

v.	0°-25°
32	0.308
64	0.370
128	0.408
256	0.458
512	0.476
1024	0.489

Table LXVI. Temperature Coefficients of Conductivity of
Lithium Nitrate in Methyl Alcohol (25, 50, and
75 per cent) and Water.

v.	25%	50%	75%
32	1.25	0.97	0.82
64	1.30	1.01	0.86
128	1.35	1.06	0.92
256	1.37	1.11	0.99
512	1.42	1.15	1.04
1024	1.46	1.16	1.07

Table LXVII. Temperature Coefficients of Conductivity of
Lithium Nitrate in Ethyl Alcohol (50 per cent)
and Water.

v.	0°-25°
32	0.83
64	0.88
128	0.91
256	0.97
512	0.99
1024	1.04

Table LXVIII. Comparison of the Molecular Conductivity of
Lithium Nitrate in Methyl Alcohol, Water,
and Mixtures of these at 0°.

v.	0%	25%	50%	75%	100%
32	50.00	29.15	23.59	26.67	45.97
64	51.49	29.58	24.49	27.95	50.12
128	51.51	30.15	25.03	28.66	53.95
256	53.40	30.70	25.71	29.51	56.67
512	54.70	31.35	26.35	30.64	60.06
1024	55.30	31.56	27.35	31.91	63.40

Table LXIX. Comparison of the Molecular Conductivity of
Lithium Nitrate in Methyl Alcohol, Water,
and Mixtures of these at 25°.

v.	0	25%	50%	75%	100%
32	91.83	60.56	47.87	47.06	63.51
64	94.62	62.16	49.92	49.52	69.32
128	98.00	63.77	51.50	51.64	74.51
256	99.68	64.96	53.57	54.36	80.57
512	101.3	66.78	54.62	56.68	83.31
1024	102.3	69.02	55.60	58.56	86.46

These values when plotted give curves very similar to those already described in connection with potassium iodide and strontium iodide. The only difference worthy of special mention is the fact that at 0° the molecular conductivity in methyl alcohol rises above that in water.

Plate VI

Curves
Showing Relation
between
Conductivity
of
Solutions
of
Lithium Nitrate
in
Water, Methyl Alcohol
and
Mixtures
at
0°C.

Curve I, $V = 32$
 II, $V = 64$
 III, $V = 128$
 IV, $V = 256$
 V, $V = 512$
 VI, $V = 1024$

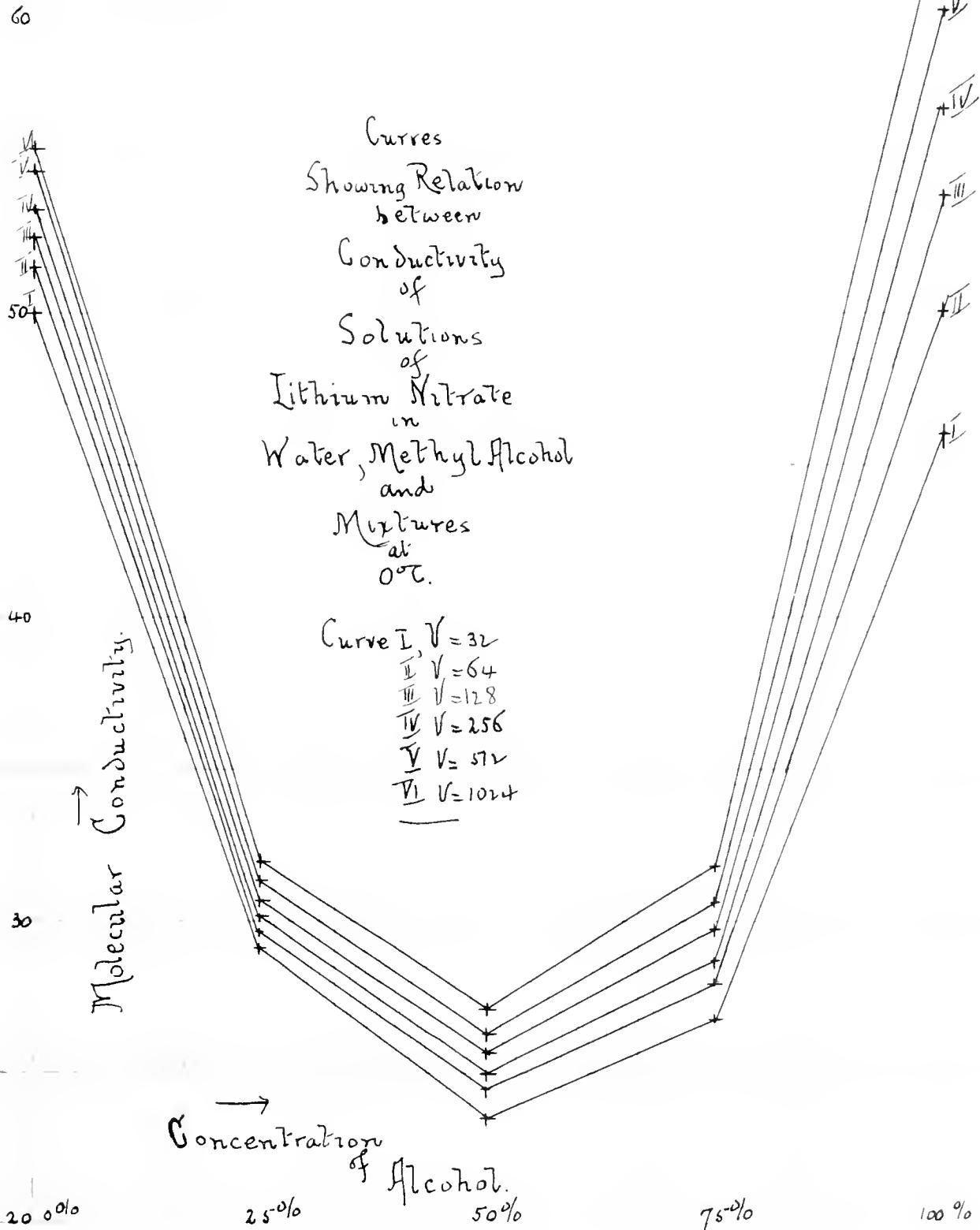
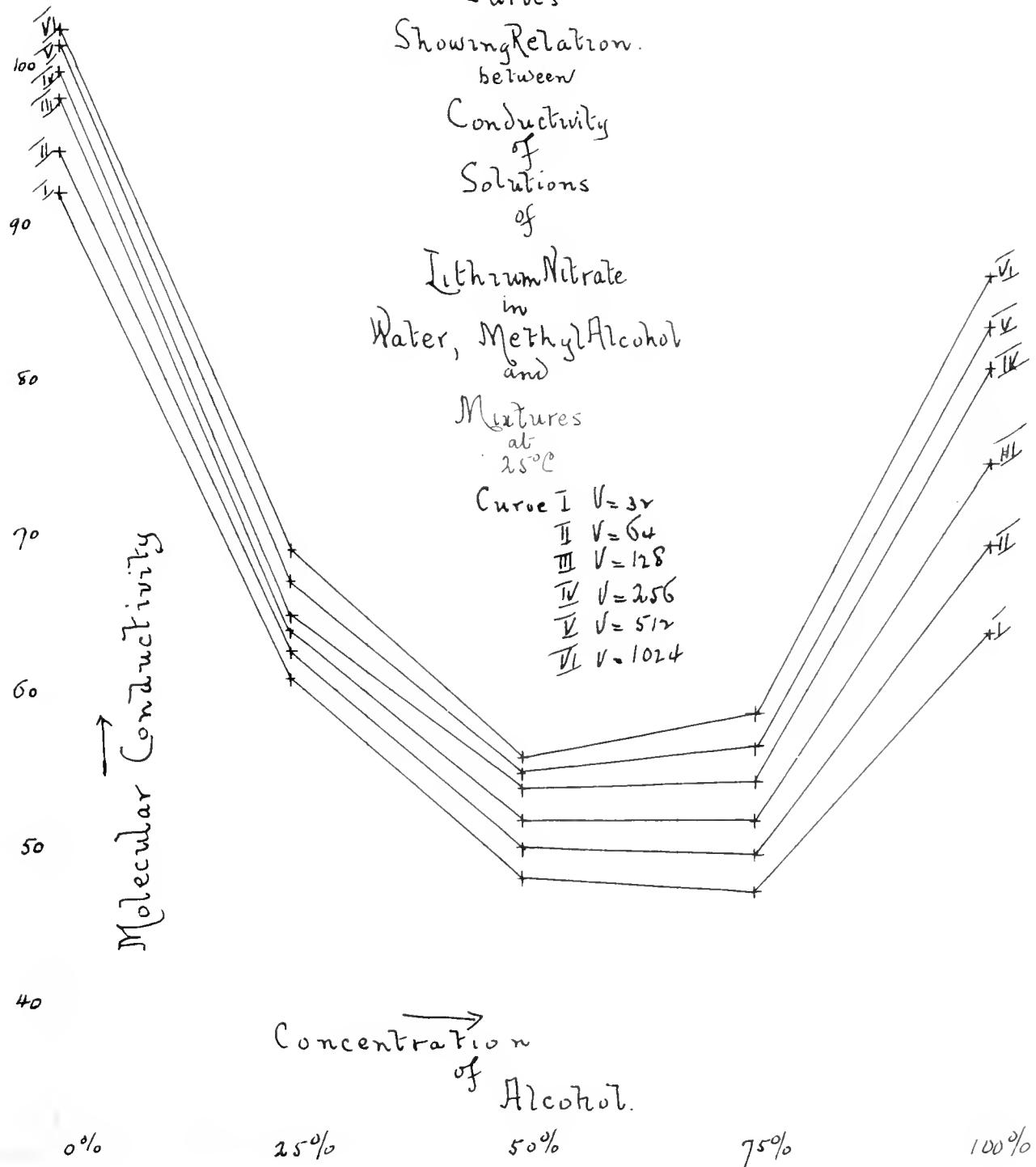


Plate VII

Curves
Showing Relation.
between
Conductivity
of
Solutions
of
Lithium Nitrate
in
Water, Methyl Alcohol
and
Mixture
at
 25°C

Curve I $V = 32$
 II $V = 64$
 III $V = 128$
 IV $V = 256$
 V $V = 512$
 VI $V = 1024$



FERRIC CHLORIDE.

It was desired to make a complete investigation of the changes in the conductivity of solutions of ferric chloride in the various solvents. This was desirable on account of the great solubility of the substance in the different alcohols and because of the large number of ions into which it can dissociate. This investigation on account of the difficulties met with and the time at my disposal has had to be postponed.

Some few measurements were however made and these are given. The ferric chloride was prepared as follows: Iron filings, which had been washed with alcohol and ether to remove any adhering grease, were heated in a large hard glass combustion tube in a current of pure dry chlorine. The ferric chloride formed was allowed to distil into a cooled portion of the tube whence it was redistilled into a wide mouthed salt bottle. The excess of chlorine was removed by heating the chloride in a current of pure dry nitrogen. The chloride thus prepared dissolved completely in both water and alcohol.

Water solutions were titrated as follows: They were reduced with zinc and sulphuric acid and the ferrous iron determined with standard permanganate. Alcoholic solutions were first precipitated with aqueous ammonia, filtered, washed, dissolved in a little hydrochloric acid, reduced and titrated as above.

Table LXV. Molecular Conductivity of Ferric Chloride
in Water.

Ferric Chloride, FeCl_3 , Molec. Wt., 162.35

v.	μ_{v0°	μ_{v25°
32	163.7	319.2
64	187.0	370.2
128	213.0	422.6
256	240.0	476.7

These values agree with those of Goodwin (1), but are in all cases slightly lower due possibly to the fact that my solutions were measured immediately after standardizing while Goodwin's had been made up for several months. Accurate measurements at a dilution greater than $V=256$ were unable to be made as hydrolysis to a very marked extent took place as noticed by Goodwin in the work just quoted

Table LXXI. Temperature Coefficient of Conductivity of Ferric Chloride in Water.

v.	$0^\circ - 25^\circ$
32	6.22
64	7.32
128	8.58
256	9.47

In mixtures of the alcohols and water the same hydrolysis was found to take place, while in the absolute alcohol solutions a different change was found to take place. The solution originally of a pale straw color became gradually lighter and lighter when in contact with the platinum black of the elec-

-trodes. This was accompanied by a steady rise in the molecular conductivity which at the end of twenty-four hours was still appreciable. The colorless solution showed but the slightest trace of ferric iron having, apparently, been reduced to the ferrous condition. These changes are shown in the following tables.

Table LXII. Table showing the Changes in the Molecular Conductivity of Ferric Chloride ($V=512$) with Time in a Mixture of Methyl Alcohol (50 per cent) and Water.

725°
12.35 P.M., April 8th.

12.27	130.1
12.29	135.6
12.31	141.~
12.33	145.4
12.36	150.8
12.38	153.9
12.41	156.3
12.45	159.5
12.56	162.4
1.00	166.7
1.10	169.1
1.30	172.3
2.00	175.0
3.00	180.6
4.00	182.2
5.00	183.0

Table LXIII. Table showing the Changes in the Molecular
Conductivity of Ferric Chloride ($V=512$)
with Time in Methyl Alcohol.

2.15 P.M. April 15th.,	$\mu_v 25^\circ$
2.18	62.90
2.21	65.47
2.24	67.18
2.28	68.16
2.35	69.64
2.45	71.91
3.00	75.00
3.15	78.06
3.30	81.75
3.45	84.11
4.15	88.59
4.45	92.93
6.15	103.6
10.30 A.M. April 16th.,	132.6
11.15	133.7
2.35 P.M.	134.3

SUMMARY.

We are led from the preceding study to conclude that the minimum point, made evident by the work of Zelinsky and Krapiwin, is not an isolated phenomenon restricted to the mixtures of methyl alcohol and water, but is much more general. This minimum point in the conductivity has been found for all the salts worked with in mixtures of methyl alcohol and water with the exception of cadmium iodide. Ethyl Alcohol and water yield a minimum in the conductivity in all the salts investigated at 0°. At 25° this minimum had disappeared. Mixtures of methyl alcohol and ethyl alcohol do not exhibit this phenomenon but the conductivity of a dissolved salt in a mixture of methyl (50 per cent) and ethyl alcohols is less than the mean of the conductivities of the substance in the pure solvents at the same dilution.

To explain these facts I would advance tentatively the following idea. According to the theory of Dutoit and Aston it is only those substances whose molecules are polymerized that can themselves dissociate dissolved electrolytes. If this be true it is probable that, since those substances which dissociate dissolved electrolytes also show in general a normal molecular weight for dissolved non-electrolytes; that this breaking down of the polymerized molecule can only be accomplished by another associated molecule. If this be true it follows that the effect of mixing two associated solvents would be to lower the state of association of both until a state of equilibrium was reached. Such a mixture would be that of water and either methyl or ethyl alcohol or a mixture

of methyl alcohol and ethyl alcohol. In these cases since the molecules are less associated than the constituents we would expect a conductivity lower than that required by the law of mixtures. In the solvents with which I have worked this is exactly what has been observed in every case. In the mixtures of methyl alcohol and water where the association of the constituents is the greatest the lowering is also the greatest as we would expect.

The effect of temperature on these lowerings has also been established since the effect of temperature is of itself to lower the state of aggregation; it would be expected that at the higher temperature the influence of the solvents on one-another would be less than at the lower. This is what has been found at 0° and 25°.

In conclusion I desire to thank Mr. Kaufman G. Falk for help in taking measurements during the latter part of the investigation.



